COATINGS. ENAMELS

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THE FLUXING EFFECT OF MINERAL MATERIAL – CULLET COMPOSITIONS ON ENAMEL GLASS

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Enamel glasses are synthesized based on the $Na_2O – B_2O_3 – Co_2O_3 – SiO_2$ system, including perlite, nepheline concentrate, and cullet. The physicochemical and technological properties of the resulting glasses and one-layer coatings based on these glasses are considered. A comparative analysis of the fluxing effect of the nepheline - cullet and perlite-cullet compositions on glasses is carried out. The reference composition areas are shown to be suitable for the development of one-coat powdered glass enamels.

The need for saving fuel and power resources in the enameling industry encourages the development of enamels with a decreased firing temperature. However, a decrease in the firing temperature due to an increased concentration of alkaline oxide impairs chemical resistance, i.e., the anticorrosion properties of the coating. One of the most promising ways for meeting this objective is introducing fluxing additives into enamel glass compositions, such as cullet, alkali-containing volcanic rocks (perlite, andesite), whose activity is determined by their vitreous structure [1], and nepheline. As a consequence of research [2 – 4], the optimum compositions of the fluxing components for addition into mixtures for cast tiles and other refractory clay products were determined.

The present study is dedicated to studying the fluxing effect of mineral material – cullet compositions on the technological and physicochemical properties of glass enamel coatings for protecting steel articles from corrosion.

The system selected for investigation was $Na_2O – B_2O_3 – Co_2O_3 – SiO_2$, which is the basis for the synthesis of one-coat enamel coatings. The system included fluxing compositions that consisted of concentrated nepheline – cullet and perlite – cullet in the following ratios of perlite (P) or nepheline concentrate (Nec) to cullet (Cul): 20/80, 30/70, 40/60, and 50/50.

Two sections of the vitreous system were investigated: $x\mathrm{Na_2O} \cdot 10\mathrm{B_2O_3} \cdot \mathrm{Co_2O_3} \cdot 50\mathrm{SiO_2} \cdot y\mathrm{Nec}/z\mathrm{Cul}$ and $x\mathrm{Na_2O} \cdot 10\mathrm{B_2O_3} \cdot \mathrm{Co_2O_3} \cdot 50\mathrm{SiO_2} \cdot y\mathrm{P}/z\mathrm{Cul}$, where x varied from 10 to 20% (here and elsewhere weight content). Cobalt oxide in the amount of 1% was introduced above 100%.

The glass batches were prepared from quartz sand of the Loevskoe deposit, nepheline concentrate from the Kirovskoe deposit, perlite from the Aragatskoe deposit, crushed window cullet from the Gomel Works (Table 1), and chemical reactants of the “pure” grade.

The enamel glasses were melted in 200 ml porcelain crucibles in an electric furnace with Silite heaters at 1350°C for 20 min.

The chemical resistance of glasses in 10% HCl and 1 N NaOH was determined by the granular method based on the weight loss of the sample after treating glass of 0.25 – 0.50 mm fraction heated over a water bath (98°C) for 1 h. The glass powders were spray-deposited on metal through a No. 006 – 009 sieve (GOST 6613–77). The firing temperature and the quality of coatings were determined after trial enameling of samples made of 08kp steel, the melting start temperature was determined by the gradient method, the spreadability at 860°C was determined according to OST 26-01-198–79, and heat resistance by OST 26-01-105–78.

TABLE 1

Material	Mass content, %					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$(Na_2O + K_2O)$
Perlite	73.65	12.97	1.40	1.12	0.20	6.76
Cullet	71.85	2.05	–	6.65	4.13	14.86
Nepheline concentrate	44.25	29.19	4.04	1.16	0.74	19.70

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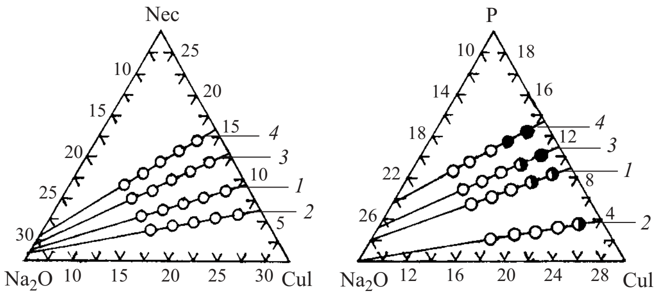

Fig. 1. Melting properties of glasses of $Na_2O – B_2O_3 – Co_2O_3 – SiO_2$ system with additives of nepheline concentrate (Nec), perlite (P), and cullet (Cul) with Nec/Cul and P/Cul ratios equal to 30/70 (*1*), 20/80 (*2*), 40/60 (*3*), and 50/50 (*4*): ○) melted; ◑) partly unmelted; ●) not melted.

In each of the two systems (Fig. 1), four sections were analyzed with the ratios of nepheline concentrate or perlite to cullet equal to 30/70, 20/80, 40/60, and 50/50 from the first to the fourth sections, respectively. Most glasses were well melted and clarified. A comparison of the melting properties of the glass systems including nepheline concentrate and perlite shows that introduction of perlite narrows to some extent the glass-formation area: in the section with perlite, it is restricted by 10.0 – 12.5% Na_2O, which is due to a higher content of high-melting oxides in perlite (($SiO_2 + Al_2O_3$) = 86.62%) compared with the nepheline concentrate (($SiO_2 + Al_2O_3$) = 73.44%) and a relatively low content of alkaline oxides (Table 1). The glasses of section *2* with the ratio of P/Cul = 20/80 are melted more easily.

The acid resistance of glasses in the nepheline-containing system is 98.27 – 99.87% and alkali resistance is 96.70 – 99.13%.

Trial enameling of steel samples based on the considered glasses in a gradient furnace indicated that the initial melting temperature depends mainly not on the ratio of Nec/Cul, but on the content of sodium oxide in the enamel glass. As can be seen in Fig. 2, an increased content of sodium oxide in the enamel glass composition decreases more effectively the initial melting temperature, which has a positive effect on spreadability. The spreadability of nepheline-containing glasses with a constant content of Na_2O equal to 17.5% meets the requirements of OST 26-01-198–79 only under the ratio of Nec/Cul = 50/50 (the spreadability at 860°C is 36 mm), and with a constant 20.0% content of Na_2O, the spreadability increases from 36 to 41 mm.

The optimum compositions of powdered glass enamel coatings with a firing temperature of 880°C were obtained on the basis of glasses 155n and 145n (sections *3* and *4*, respectively) containing 12.5% Na_2O. The coatings have a high mirror reflection coefficient (60 – 6%) and good parameters of alkali and acid resistance (98.42 and 99.1%).

An increase in the perlite content in the ratio to cullet does not have a fluxing effect: the initial melting temperature becomes somewhat higher (most perceptibly in the section with a constant content of Na_2O equal to 20.0%) and the spreadability virtually does not change. The spreadability of the considered perlite-containing glasses increases from 26 to 36 mm as the Na_2O content grows from 12.5 to 20.0%.

The chemical resistance of glasses of the perlite-containing system in 10% HCl is 97.8 – 99.96%, and the resistance in 1 N NaOH is 96.43 – 97.15%.

Coatings based on the perlite-bearing system with ratios of P/Cul = 40/60 (section *3*) and 50/50 (section *4*) have a great quantity of gas bubbles, which is presumably due to the high viscosity of the enamel glasses.

Thus a flux composition with constant ratios of P/Cul = 30/70 (section *2*) and 20/80 (section *1*) decreases the viscosity of the glass melts of the considered system within the temperature range corresponding to the temperature of melting of the coatings. The highest fusibility of the coatings is observed with the ratio P/Cul = 20/80.

The optimum coating was obtained on the basis of enamel glass 167n (section *4*) containing 12.5% Na_2O. The firing temperature of the coating is 880°C, the melting starting temperature 795°C, the spreadability 22 mm, and the strength of adhesion of the coating to metal 92.7%. The coating

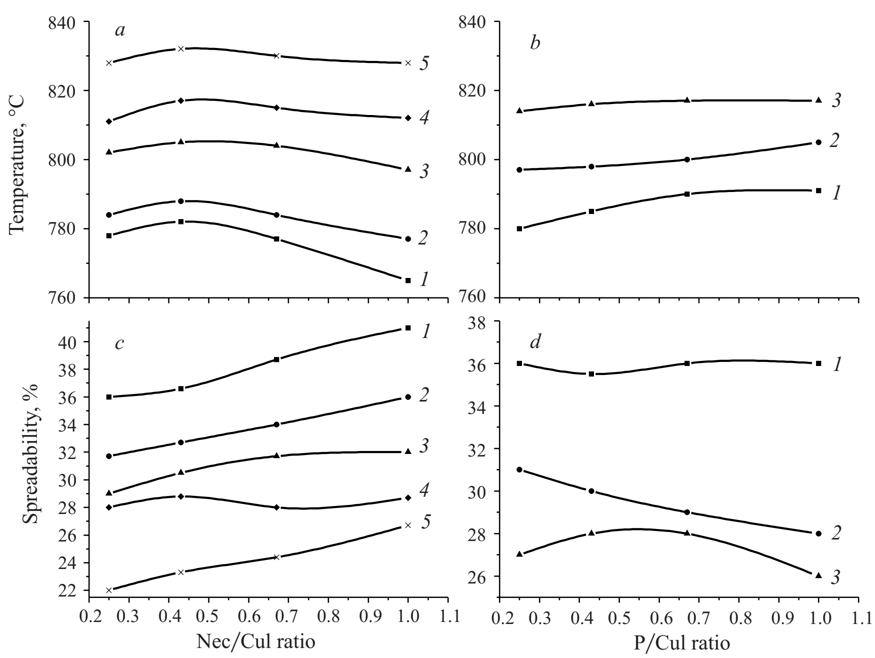

Fig. 2. Dependence of the starting melting temperature (*a*, *b*) and spreadability (*c*, *d*) in glasses of the $Na_2O – B_2O_3 – Co_2O_3 – SiO_2$ system sections with a constant Nec/Cul or P/Cul ratio equal to (20/80 = 0.25, 30/70 = 0.43, 40/60 = 0.67, 50/50 = 1.00) on the mass content of Na_2O equal to 20.0% (*1*), 17.5% (*2*), 15.0% (*3*), 12.5% (*4*), and 10.0% (*5*).

TABLE 2

Enamel	Section	Melting start temperature, °C	Spreadability at 860°C, mm	Chemical resistance, %	
				in 10% HCl	in 1 N NaOH
$Na_2O – B_2O_3 – Co_2O_3$ – *P/Cul* – SiO_2 *System*					
175n	1	800	30.2	99.55	96.50
180n	2	798	33.1	99.30	96.43
170n	3	804	29.9	99.54	96.60
165n	4	807	27.3	99.59	96.96
$Na_2O – B_2O_3 – Co_2O_3$ – *Nec/Cul* – SiO_2 *System*					
157n	1	785	32.0	98.52	96.79
162n	2	790	30.0	98.95	96.69
152n	3	780	35.5	–	97.13
147n	4	775	37.3	98.27	–

has high acid resistance 99.96% and heat resistance (400 – 20°C).

A comparative analysis of the chemical and technological properties of nepheline- and perlite-bearing enamels glasses and coatings based on them in the section containing 17.5% Na_2O (Table 2) indicated that the nepheline-containing glasses of the considered system have higher spreadability and a lower melting temperature of the coatings, whereas the perlite-containing glasses have higher acid resistance.

As a result of the performed studies, the reference composition ranges suitable for the development of anti-corrosion one-coat powder glass enamels are identified, and the optimum ratios of nepheline : cullet and perlite : cullet are determined, which have the best effect on increasing the fusibility of glasses and their chemical resistance.

REFERENCES

1. I. G. Khizanishvili and G. S. Gverdtsiteli, “Volcanic rocks as main glass-forming materials in production of enamels,” in: *Glass Enamel and Enameling of Metals, Issue 1* [in Russian], Novocherkassk (1974), pp. 94 – 97.
2. K. V. Dazhuk and A. V. Mishchenko, “Concentration waste as a valuable material for producing facing ceramic tiles,” *Steklo Keram.*, No. 7, 34 – 37 (1971).
3. M. G. Lundina, K. I. Rostovtseva, and T. A. Danilevich, “Development of technological parameters of mixtures and glaze compositions for production lines for facing ceramics,” in: *Publ. of NIIstroikeramika Institute, Issue 27* [in Russian], pp. 145 – 158 (1967).
4. M. É. Kats and K. G. Kvyatkovskaya, “Low-temperature flux compositions for production of cast ceramic tiles,” *Steklo Keram.*, No. 2, 22 – 23 (1972).